



CuInS₂ sensitized TiO₂ hybrid nanofibers for improved photocatalytic CO₂ reduction

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ABSTRACT

Photocatalytic CO₂ reduction into solar fuels over photocatalysts has theoretically and practically become a hot research topic. Herein, we fabricated a novel hybrid TiO₂ nanofiber coated by CuInS₂ nanoplates through a hydrothermal method. The materials were characterized by X-ray diffraction, electron microscopes, UV-vis absorption spectra, nitrogen sorption, X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy. The resulting TiO₂/CuInS₂ hybrid nanofibers exhibit superior photocatalytic activity for CO₂ reduction under irradiation, due to the generation of direct Z-scheme heterojunction between TiO₂ and CuInS₂. This work may provide an alternate methodology to design and fabricate multicomponent TiO₂-based photocatalyst for high-efficiency CO₂ photoreduction.

1. Introduction

Photocatalytic CO₂ reduction over well-designed catalysts has been considered an emerging way for recycling CO₂ back to renewable fuels, *e.g.*, CH₄ and CH₃OH with the aid of solar energy, which is regarded as one of the most promising strategies to overcome the energy and environmental crises [1–7]. For example, metal-organic frameworks (MOF), a type of micro-mesoporous hybrid materials, are recently emerging as a new category of materials for CO₂ photo-reduction due to their special structural characteristics and remarkable adsorption capability for CO₂ [8–10]. Besides, TiO₂ as a typical semiconductor photocatalyst, has been frequently studied for CO₂ reduction due to its high stability, nontoxicity and abundant availability [11–14]. However, TiO₂ can only absorb UV-light because of its large band gap [15,16]. Moreover, it shows a fast recombination of the photogenerated electron-hole pairs, which leads to low photocatalytic performance [17–19]. Several approaches have been explored to improve the photocatalytic activities of TiO₂, including noble metal deposition (*e.g.* Pt, Au, Pd, Ag) [20–24], nonmetal doping (*e.g.* N, C) [25–28], surface sensitization [29,30], coupling with narrow-bandgap semiconductors (*e.g.* CdS, g-C₃N₄, Cu₂O) [31–36] and so on. Among these, hybridizing TiO₂ with other semiconductors is believed to be an effective method to broaden the light absorption and meanwhile improve the separation

and extraction of the photogenerated carriers.

Differing from TiO₂, CuInS₂ has a narrow direct band gap of 1.50 eV, close to the optimal band gap (1.45 eV) for solar light harvesting [37–39], and meanwhile shows an ultrahigh absorption coefficient ($1 \times 10^5 \text{ cm}^{-1}$). Besides, CuInS₂ shows a pronounced defect tolerance and exceptional radiation hardness as compared to other semiconductors [40–42]. CuInS₂ does not contain any toxic heavy metals and has been investigated for photovoltaics [43], bioimaging [44], and photocatalytic water splitting [45]. For instance, Kudo and coworkers have prepared a ZnS-CuInS₂-AgInS₂ ternary solid solution which exhibited 7.4% quantum yield of hydrogen production under 520 nm irradiation [45]. In addition, CuInS₂ has been combined with other semiconductors to make composite photocatalysts, such as MoS₂/CuInS₂ [46], g-C₃N₄/CuInS₂ [47], Bi₂WO₆/CuInS₂ [48] and ZnO/CuInS₂ [49,50], for enhanced H₂ generation from water splitting or organic pollutants degradation. In these cases, CuInS₂ was presented as nanosheets or quantum dots. It is also reported that CuInS₂ thin films can function as cathodes for photoelectrochemical reduction of CO₂ [51]. However, CuInS₂ involved photocatalysts for direct CO₂ reduction have been rarely demonstrated and more efforts are required to improve the solar driven CO₂-to-fuel conversion efficiency.

Herein, we report the facile synthesis of TiO₂ nanofibers sensitized with CuInS₂ nanoplates through an *in-situ* hydrothermal process. The

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obtained $\text{TiO}_2/\text{CuInS}_2$ hybrid nanofibers show increased optical absorption and enhanced charge separation, and thus improved photocatalytic CO_2 reduction was achieved. Based on the experimental data and DFT calculation, we propose a direct Z-scheme heterojunction formed between the TiO_2 nanofiber and the CuInS_2 nanoplates.

2. Experimental details

2.1. Materials and synthesis of electrospun TiO_2 nanofibers

Poly(vinyl pyrrolidone) with an average molecular weight of 1,300,000 was purchased from Tianjin Bodi Chemical Co., Ltd. The other chemicals were of analytical grade and purchased from Shanghai Chemical Company. Electrospun TiO_2 nanofibers were prepared according to our previous work [11]. Typically, 2.0 g of Tetraethyl titinate (TBT) and 0.75 g of PVP were dissolved in the solvent containing 10.0 g of ethanol and 2.0 g of acetic acid. The mixture became a transparent light yellow solution after magnetically stirring for 5 h at room temperature. The solution was then poured into a 10 mL syringe in the electrospinning setup. The steel needle had a distance of 10 cm and a voltage of 15 kV with respect to the static collector. And the solution feeding rate is maintained at 2.5 mL h⁻¹. The collected electrospun samples (TiO_2 precursors) were calcined at 550 °C in air for 2 h with a ramping rate of 2 °C min⁻¹.

2.2. Preparation of $\text{TiO}_2/\text{CuInS}_2$ heterostructures

TiO_2 nanofibers were first chemically etched to increase surface roughness. Briefly, TiO_2 nanofiber was immersed in a concentrated NaOH solution (10 M) at 160 °C for 15 min, and washed with dilute HCl solution and water for several times. As-etched TiO_2 fibers were then annealed at 450 °C in air for 1 h with a ramping rate of 2 °C min⁻¹. The rough TiO_2 nanofibers are labeled as T.

$\text{TiO}_2/\text{CuInS}_2$ heterostructures were synthesized through a hydrothermal method. Typically, a transparent solution was formed by mixing 0.0125 mmol $\text{Cu}(\text{NO}_3)_2$ (the mass ratio of CuInS_2 was 1 wt. %), 0.0125 mmol $\text{In}(\text{NO}_3)_2$ and 0.025 mmol L-cysteine hydrochloride with 80 mL deionized water. Then 0.1 g TiO₂ nanofibers were added to the above solution under vigorous stirring. The obtained suspension was transferred to a Teflon cup of 100 mL inner volume in a stainless steel-lined autoclave. The autoclave was maintained at 160 °C for 12 h and then was allowed to cool to room temperature. The solid product was washed with deionized water and ethanol several times and dried at 80 °C for 4 h to obtain $\text{TiO}_2/\text{CuInS}_2$ heterostructures. For comparison, $\text{TiO}_2/\text{CuInS}_2$ samples with various mass ratios of CuInS_2 were synthesized by varying the amount of $\text{Cu}(\text{NO}_3)_2$ from 0.03, 0.06 to 0.12 mmol while fixing the molar ratio of $\text{Cu}(\text{NO}_3)_2 : \text{In}(\text{NO}_3)_2 : \text{L-cysteine hydrochloride}$ at 1:1:2. The nominal mass ratios of CuInS_2 were 2.5 wt. %, 5 wt. % and 10 wt. %, respectively. These $\text{TiO}_2/\text{CuInS}_2$ samples were labeled as TC_x ($x = 1, 2.5, 5, 10$). The actual compositions of the samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) by using a Prodigy 7 spectrometer (see Table 1)

Table 1
Physical properties of the samples.

Samples	CuInS_2 (mol%)	S_{BET} (m ² /g)	PV (m ³ /g)	APS (nm)
T	–	43	0.14	10
TC1	1.4	68	0.18	10.4
TC2.5	3.1	102	0.45	17.6
TC5	5.2	83	0.45	21.5
TC10	9.4	51	0.25	20.1

PV: pore volume, APS: average pore size.

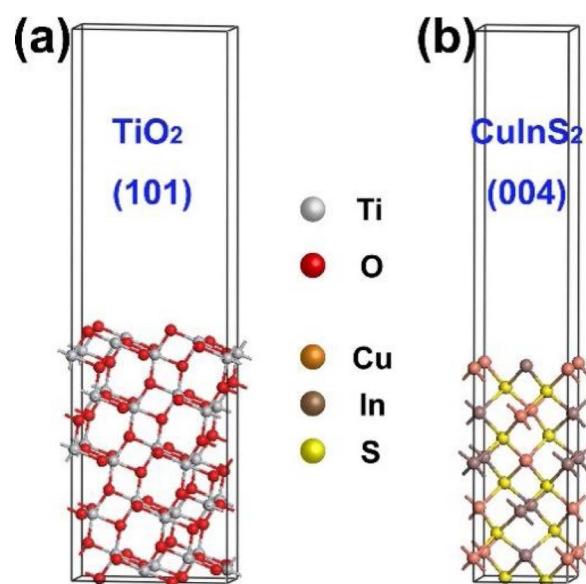


Fig. 1. Geometric structure of (a) TiO_2 (101) surface and (b) CuInS_2 (004) surface. The grey, red, orange, brown and yellow spheres stand for Ti, O, Cu, In and S atoms, respectively.

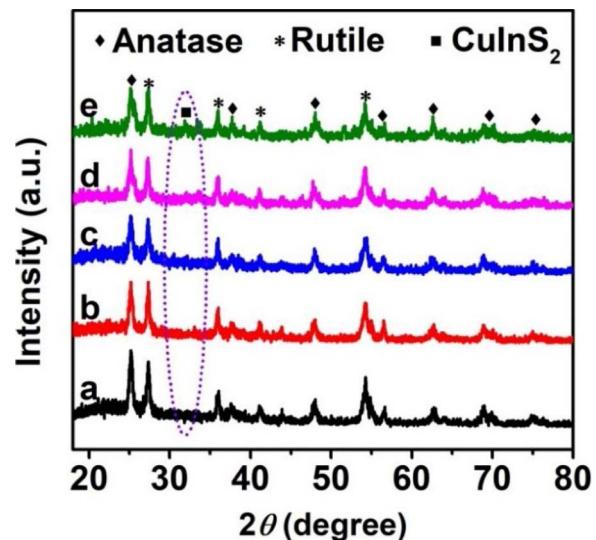


Fig. 2. XRD patterns of the samples: (a) T, (b) TC1, (c) TC2.5, (d) TC5 and (e) TC10. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

2.3. Characterization

The X-ray diffraction (XRD) patterns were recorded on a D/Max-RB X-ray diffractometer (Rigaku, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418$ nm) with a scan rate (2θ) of 0.05° s⁻¹. The morphology was observed on a JSM 7500F field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) images and energy dispersive X-ray (EDX) spectrometer were recorded on a Titan G2 60–300 electron microscope. Nitrogen adsorption-desorption data were recorded on a Micromeritics ASAP 3020 nitrogen adsorption apparatus (USA) at 77 K. Prior to measurements, the samples were degassed at 150 °C for 12 h. The specific surface areas (S_{BET}) calculated by the Brunauer-Emmett-Teller (BET) method using adsorption data in a relative pressure range from 0.05 to 0.3. The total pore volumes were estimated from nitrogen adsorption volume adsorbed at the relative pressure of 0.97. The pore size distributions were calculated from desorption data of isotherms using the Barret-Joyner-Halender (BJH)

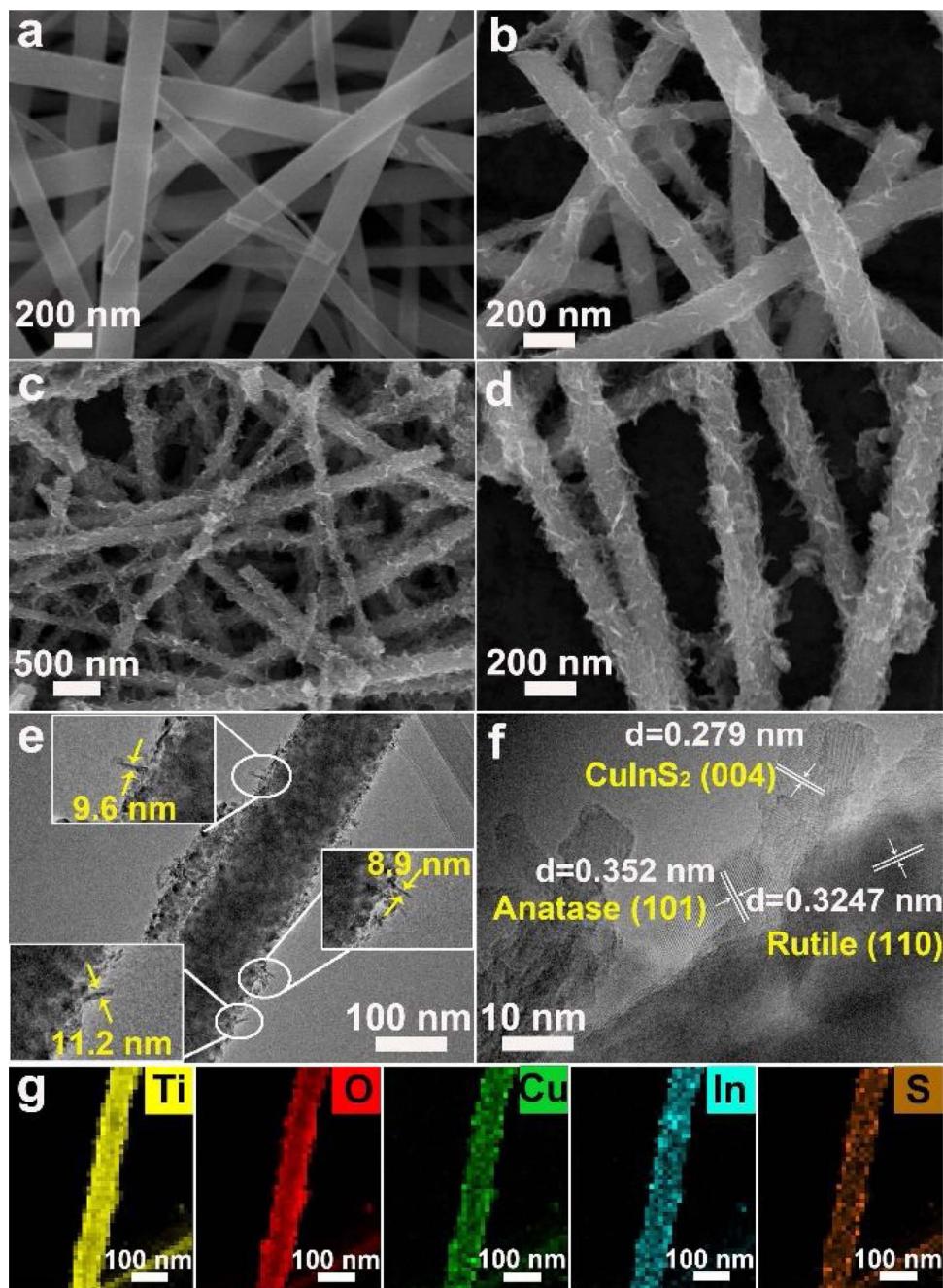


Fig. 3. SEM images of (a and b) T and (c and d) TC2.5. TEM image (e) and HRTEM image (f) of TC2.5. EDX element mappings of (g) Ti, O, Cu, In and S elements for TC2.5.

method. UV-vis diffuse reflectance spectra of samples were recorded on a Shimadzu UV-2600 UV-vis spectrophotometer (Japan) using BaSO_4 as a reference. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo ESCALAB 250Xi instrument with Al K_α X-ray radiation. The binding energy was calibrated with reference to C 1s signal (284.8 eV).

2.4. Photoelectrochemical measurements

The photoelectrochemical measurements were conducted in 0.5 M Na_2SO_4 aqueous solution on a CHI660C electrochemical workstation (Shanghai CH Instruments), with a 3 W LED lamp (365 nm) as the light source. A Pt wire and saturated Ag/AgCl electrode were used as counter and reference electrodes, respectively. For preparing the working electrode, 80 mg of the photocatalysts (T, TC1, TC2.5, TC5 and TC10)

were ground with 1.0 mL ethanol to form a slurry. The slurry was blade-coated onto a 2 cm \times 1.5 cm F-doped SnO_2 -coated (FTO) glass with an active area of 1 cm^2 , followed by drying at 100 °C for 1 h. All the electrodes used had a similar thickness. The EIS measurements were carried out by applying the bias of the open circuit potential and recorded over a frequency range of 0.01–10⁵ Hz with an ac amplitude of 10 mV.

2.5. Analysis of hydroxyl radicals ($\cdot\text{OH}$)

A terephthalic acid (TA) fluorescence probe method was used to quantitatively analyze the production of $\cdot\text{OH}$. Typically, 0.1 g of photocatalyst was dispersed in a 20 mL solution containing 0.5 mM TA and 5 mM NaOH. The suspension was placed in a dish with a diameter of 9 cm. A 350 W Xe arc lamp (Zhenjian Silver Jewelry Chemical, China)

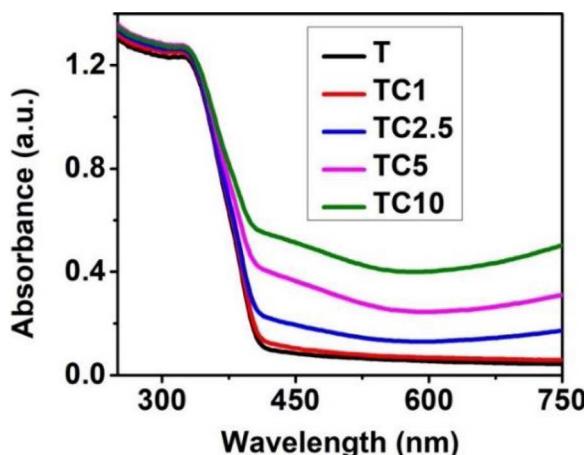


Fig. 4. Diffuse reflectance spectra of the samples.

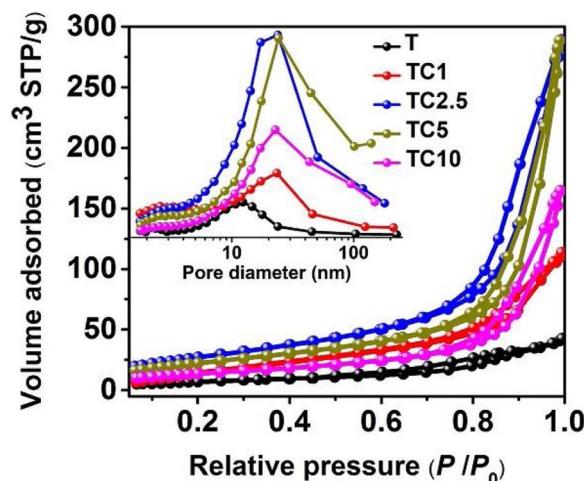


Fig. 5. Left: nitrogen adsorption-desorption isotherms (inset: pore size distributions) of the samples. Right (Table 1): specific surface area (S_{BET}), pore volume (PV) and average pore size (APS) derived from the isotherms.

was positioned 25 cm above the dish. The light intensity on the solution was measured to be 2.0 mW cm^{-2} with a UV radiometer with the peak intensity of 365 nm (model: UV-A, Photoelectric Instrument Factory of Beijing Normal University). TA easily reacts with $\cdot\text{OH}$ and produces a highly fluorescent 2-hydroxyterephthalic acid (TAOH). The amount of $\cdot\text{OH}$ was determined by measured the concentration of TAOH (fluorescence peak at 425 nm with an excitation wavelength of 315 nm) using a Hitachi F-7000 fluorescence spectrophotometer after centrifugation.

2.6. Photocatalytic reduction of CO_2

The photocatalytic reduction of CO_2 was carried out in a 200 mL home-made Pyrex reactor with two openings. A 350 W simulated solar Xe arc lamp was used as the light source and positioned 10 cm above the reactor. A suspension was firstly placed in the reactor by ultrasonically mixing 50 mg of the catalyst and 10 mL of deionized water. After drying at 80°C for 2 h, the catalyst formed a uniform film coating on the bottom of the reactor. Prior to irradiation, the reactor was purged with nitrogen for 30 min to ensure an anaerobic circumstance. CO_2 together with H_2O vapor was in-situ produced through the reaction of NaHCO_3 (0.12 g, introduced into the reactor before seal) and the injected H_2SO_4 solution (0.25 mL, 2 M). The product (1 mL) was automatically collected at given intervals (1 h) and analyzed using a Shimadzu GC-2014C gas chromatograph (Japan) equipped with an FID detector and a methanizer. Blank experiments in the absence of CO_2 or

light irradiation confirmed the CO_2 and light were the key factors for the CO_2 reduction. Control experiment was also performed to determine whether the carbon resource came from CO_2 .

$^{13}\text{CO}_2$ isotope tracer experiment was conducted to verify the carbon source of the products by using ^{13}C isotope-labelled sodium bicarbonate ($\text{NaH}^{13}\text{CO}_3$, Cambridge Isotope Laboratories Inc., USA) and H_2SO_4 aqueous solution for the photocatalytic examinations. After 1 h of photocatalytic reaction, 500 μL of mixed gas was taken out from the reactor and examined by a gas chromatography-mass spectrometer (GC-MS) (6980N network GC system-5975 inert mass selective detector, Agilent technologies, USA) to analyze the products.

2.7. Computational details

The density functional theory (DFT) calculations were performed by using the Cambridge Serial Total Energy Package (CASTEP). Generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was utilized to describe the exchange-correlation interaction. The energy cutoff and Monkhorst-Pack k-point mesh were set to as 440 eV and $7 \times 7 \times 1$, respectively. During the geometry optimization, the convergence tolerance was set as $1.0 \times 10^{-5} \text{ eV/atom}$ for energy and $0.03 \text{ eV}/\text{\AA}$ for maximum force. For the construction of surface models, a vacuum of 20 \AA was used to eliminate interactions between periodic images. The geometric structures of TiO_2 (101) surface and CuInS_2 (004) surface are illustrated in Fig. 1. The work function is defined as $\phi = E_V - E_F$, where E_V and E_F are the electrostatic potentials of the vacuum and Fermi levels, respectively.

3. Results and discussion

3.1. Crystalline phase and morphology of materials

Fig. 2 shows the XRD patterns of the resultant samples with various loadings of CuInS_2 . For the original TiO_2 nanofibers, the diffraction peaks can be assigned to anatase TiO_2 (JCPDS file No. 21-1272) or rutile TiO_2 (JCPDS file No. 21-1276). No other diffraction peaks were observed for TC1 and TC2.5 because of the quite low loading of CuInS_2 . In contrast, TC5 and TC10 which had higher loadings of CuInS_2 show a new diffraction peak at around 32.1° , which correspond to the (004) plane of tetragonal CuInS_2 (JCPDS file No. 85-1575). The results confirm the formation of CuInS_2 by hydrothermal deposition, which can be further verified by TEM observation below.

The morphologies of the resultant samples were investigated by SEM and TEM. The SEM image of the pristine TiO_2 before and after NaOH etching was shown in Fig. 3a and b, illustrating nanofibers with diameters around 150 nm and lengths of tens of micrometers. After the hydrothermal growth, CuInS_2 nanoplates were deposited onto the TiO_2 nanofibers, as shown in Fig. 3c and d. The very thin CuInS_2 nanoplates had high surface area and more active sites can be exposed, which will be highly favourable for the photocatalytic reactions. The microstructure of the $\text{TiO}_2/\text{CuInS}_2$ hybrid can be further revealed by TEM image (Fig. 3e), showing a TiO_2 nanofiber coated by CuInS_2 nanoplates with thickness of *ca.* 10 nm.

The crystalline phase of the hybrid material was also examined by high-resolution TEM (HRTEM). As shown in Fig. 3f, the lattice fringes with a spacing of 0.352 and 0.324 nm corresponded to the (101) plane of anatase TiO_2 and (110) plane of rutile TiO_2 , respectively. In addition, lattice fringes with a spacing of 0.279 nm were also observed, which was attributed to the (004) plane of CuInS_2 . The HRTEM analysis further confirmed the generation of CuInS_2 over the TiO_2 nanofibers, agreeing with the XRD results as above. The EDX mapping (Fig. 3g) of the nanofiber indicates the co-existence of Ti, O, Cu, In and S elements, resulting from the heterostructured $\text{TiO}_2/\text{CuInS}_2$ composite.

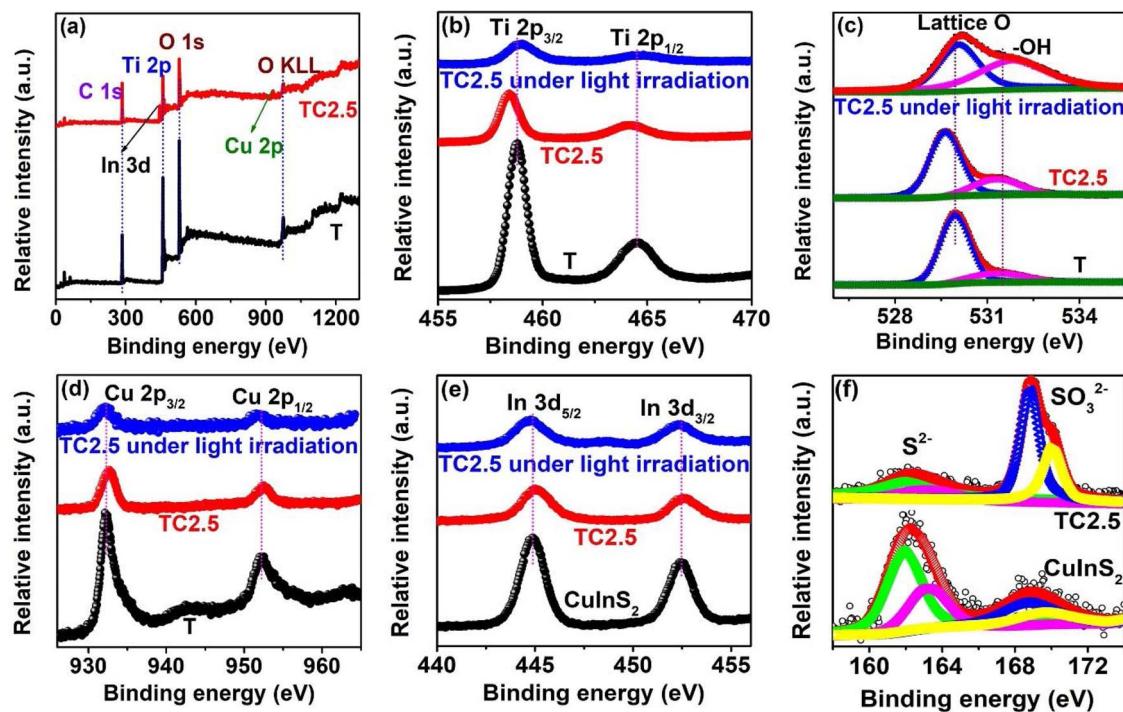


Fig. 6. (a) XPS survey spectra of T and TC2.5. XPS spectra of (b) Ti 2p and (c) O 1s of T and TC2.5. XPS spectra of (d) Cu 2p, (e) In 3d and (f) S 2p of CuInS₂ and TC2.5.

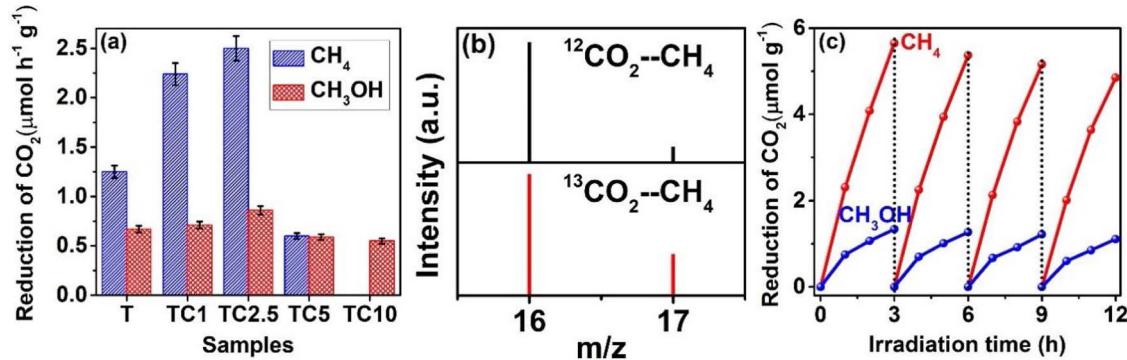


Fig. 7. (a) Photocatalytic activities of the CO₂ reduction over different photocatalysts. (b) The GC-MS patterns of the produced CH₄ over TC2.5 using ¹²CO₂ and ¹³CO₂ as the carbon source, respectively. (c) The long-term photocatalytic activities of TC2.5 for CO₂ reduction.

3.2. UV-vis absorption and nitrogen sorption

UV-vis diffuse reflectance spectra were measured to study the optical absorption properties of the samples, as shown in Fig. 4. As expected, the pristine TiO₂ sample can only absorb UV light (wavelength below 400 nm). After deposition of CuInS₂, the hybrid nanofibers show enhanced visible-light absorption with the increased loading of CuInS₂, resulting from the low bandgap and strong absorption capability of the CuInS₂ nanoplates. The significantly improved optical absorption of the hybrid can potentially result in higher photocatalytic activity for CO₂ reduction, as described below.

Fig. 5 shows the nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) for T, TC1, TC2.5, TC5 and TC10. All the isotherms can be identified as type IV according to the BDDT (Brunauer, Deming, Deming and Teller) classification and having H3-type hysteresis loops at P/P_0 between 0.45 and 0.9, indicating the presence of narrow slit-shaped mesopores that may originate from the random distribution of CuInS₂ nanoplates on the TiO₂ nanofibers [52]. The inset of Fig. 5 shows the corresponding pore size distributions of the samples calculated according to the desorption isotherms. All the samples show mesoporous structures with the pore

size increasing from ~10 nm to ~20 nm after the coating of to the CuInS₂ nanoplates. Table 1 summarizes the specific surface areas (S_{BET}), pore volumes and pore sizes of the samples. The S_{BET} of the samples shows a volcano shape and reaches the maximum value of 102 m² g⁻¹ for TC2.5, as the loading of CuInS₂ was increased.

3.3. XPS analysis

The surface composition and chemical states of the resultant samples were investigated by XPS. The survey XPS spectrum (Fig. 6a) shows the presence of Cu and In elements for TC2.5, in addition to Ti and O, confirming the generation of CuInS₂. Fig. 6b shows the high-resolution Ti 2p spectrum with two symmetrical peaks corresponding to Ti 2p_{3/2} at 458.8 eV and Ti 2p_{1/2} at 464.5 eV, respectively. The O 1s XPS spectra of both samples (Fig. 6c) can be deconvoluted to lattice oxygen (529.8 eV) in TiO₂ and –OH species (531.6 eV). Note that the binding energies of both Ti 2p and O 1s for TC2.5 shifted by 0.5 eV to lower values as compared to T, suggesting the presence of electron transfer from CuInS₂ to TiO₂ after hybridization, which will build an internal electric field at the interface of the hybrid. The directed electron transfer between the two components of the hybrid can be further

Table 2
Photocatalytic CO₂ reduction performances of various TiO₂-based photocatalysts.

Photocatalyst	Reducant	Light	Product	Yield ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Ref.
2.5 % CuInS ₂ /TiO ₂	H ₂ O vapor	350 W Xe lamp	CH ₄	2.5	This work
CuIn ₂ S ₄ -0.33/TiO ₂	H ₂ O vapor	300 W Xe lamp	CH ₃ OH	0.86	[53]
Pt/TiO ₂	H ₂ O vapor	300 W Xe lamp	CH ₄	4.8	[54]
1.5 % Ag/TiO ₂	H ₂ O vapor	300 W Xe lamp	CO	0.1	[55]
Pt-Cu ₂ O/TiO ₂	H ₂ O vapor	300 W Xe lamp	CH ₄	1.42	[56]
Ag-Mn-N/TiO ₂	H ₂ O vapor	300 W Xe arc lamp	CO	0.05	[26]
5 wt.% GO/TiO ₂	H ₂ O vapor	500 W Xe arc lamp	CH ₄	0.5	[17]
			CO	1.86	
			C ₂ H ₆	0.05	
			C ₂ H ₄	0.51	
A/R-TiO ₂	H ₂ O vapor	100 W Xe lamp	CH ₄	1.13	[57]
TiO ₂ flakes	H ₂ O liquid	300 W Hg lamp	Formate	1.9	[58]

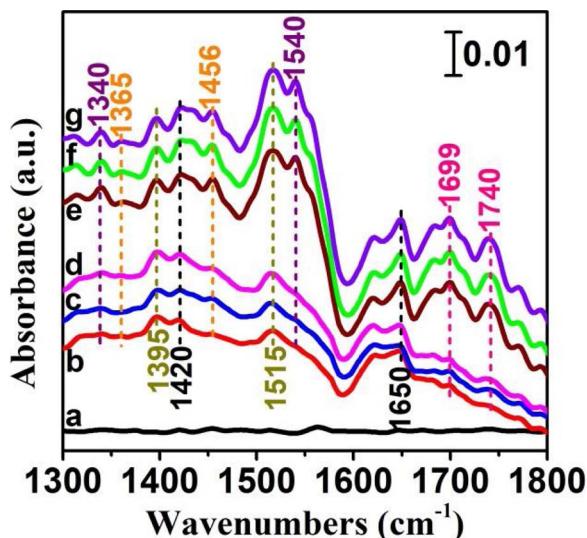


Fig. 8. *In-situ* DRIFTS spectra of TC2.5 under the flow CO₂/H₂O: (a) in the absence of CO₂/H₂O in the dark, (b–d) after the introduction of CO₂/H₂O for 20, 40 and 60 min in the dark, and (e–g) after the photo-irradiation for 20, 40 and 60 min.

verified by the DFT calculation shown below. The electron transfer and the associated electric field would play a role in the heterojunction formation and hence affect the photocatalytic activities for CO₂ reduction.

The Cu 2p XPS spectrum of TC2.5 shown in Fig. 6d contained two signals at 932.0 and 951.5 eV, corresponding to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively. The two strong photoelectron signals at 444.8 and 452.3 eV in the In 3d XPS spectrum (Fig. 6e) of TC2.5 were assigned to In 3d_{5/2} and In 3d_{3/2}, respectively. For comparison, the XPS of pure CuInS₂ were also measured and shown in Fig. 6d–f. The binding energies of Cu and In for TC2.5 showed clear shift to higher values compared to those of CuInS₂, implying the electron transfer from CuInS₂ to TiO₂, which agree with the above analysis and suggest the formation of built-in electric field and direct Z-scheme heterojunction between them, as detailed below. Fig. 6f shows the XPS signal of sulfur, which can be assigned to the presence of S^{2–} and SO₃^{2–} species.

Apparently, S^{2–} derived from the formation of CuInS₂, and SO₃^{2–} may be generated during the disproportionation of L-cysteine hydrochloride. The results further prove the existence of CuInS₂ in TC2.5, which are in good agreement with the XRD and HRTEM analyses.

3.4. Photocatalytic CO₂ reduction and *in-situ* DRIFTS measurement

For the photocatalytic CO₂ reduction tests, control experiments were first conducted in the absence of photocatalysts, carbon source, irradiation or H₂O (N₂ was used as the reference gas). We found that hydrocarbons were produced only in the presence of the photocatalysts, irradiation, H₂O and CO₂, which verified that the hydrocarbons resulted exclusively from the photoreduction of CO₂. Here, CO₂ can be reduced to CH₄ and CH₃OH upon the as-prepared materials under Xe lamp irradiation. Fig. 7a shows the yields of CH₄ and CH₃OH after 1 h of irradiation over the samples. It can be seen that the hydrocarbon yield increased with the loading of CuInS₂ and reached a maximum value over TC2.5, with the production rate of 2.5 $\mu\text{mol h}^{-1} \text{g}^{-1}$ for CH₄ and 0.86 $\mu\text{mol h}^{-1} \text{g}^{-1}$ for CH₃OH. We consider the improvements resulted from the enhanced light absorption, increased surface area and possible improved charge separation and extraction after the growth of CuInS₂. We note that the generation rate of CH₄ by TC2.5 almost doubled the generation rate by T, while the yield of CH₃OH only showed a minor increase. Further rising of the CuInS₂ amount would result in a decrease of photocatalytic efficiency (sample TC5 and TC10).

We note that the product (CH₄ and CH₃OH) distribution of CO₂ reduction over TiO₂/CuInS₂ varied with the loading amount of CuInS₂. From the thermodynamic point of view, the reduction potential of CO₂ → CH₄ (−0.24 V vs. NHE, pH7) is more positive than that of CO₂ → CH₃OH₄ (−0.38 V vs. NHE, pH7). We speculate that with increasing amount of CuInS₂, more electrons can be generated and/or transferred to react with CO₂ molecules. Meanwhile, since the CO₂ → CH₄ is energetically more favourable than CO₂ → CH₃OH₄ as mentioned above, the CH₄ generation rate was improved with the loading of CuInS₂, and meanwhile the generation rate of CH₃OH remained unchanged.

Further, to verify the real carbon source of the photocatalytic products, isotope tracer experiment involving photo-reduction of ¹³CO₂ (¹²CO₂ was also tested as a reference) was conducted and examined by GC-MS. As shown in Fig. 7b, a strong peak assigned to ¹³CH₄ (*m/z* = 17) was clearly observed when using ¹³CO₂ as the carbon source, while the corresponding peak using ¹²CO₂ as the carbon source was much weaker. These results confirmed that the detected products over the as-prepared photocatalyst originated from the CO₂ source gas rather than any residual/contaminant carbon species.

Table 2 shows the photocatalytic CO₂ reduction performance of various TiO₂-based photocatalysts. It can be found that the TiO₂/CuInS₂ hybrid exhibits higher or comparable photocatalytic CO₂ conversion activities compared with most of the recently reported TiO₂-based photocatalysts. There are few materials showing higher CO₂ reduction efficiency, nevertheless, these photocatalysts were modified with noble metals such as Pt and Ag, which increased the cost and limited the large-scale usage. Further, the long-term stability of the TiO₂/CuInS₂ hybrid was checked and we found that the photocatalytic CO₂ reduction rate was largely remained after 12 h illumination (Fig. 7c). Therefore, the easily-prepared, noble-metal-free cocatalyst of CuInS₂ can still be of great interest for achieving high-efficiency CO₂ reduction.

Further, we conducted *in-situ* DRIFTS measurement to explore the CO₂ photoreduction mechanism over TC2.5. As shown in Fig. 8, no absorption bands can be found in the absence of CO₂ and H₂O (Fig. 8a) in the dark. When CO₂ and water vapor were introduced into the reactor for 20 min in the dark, the molecules can be adsorbed onto TC2.5, evidenced by the presence of the monodentate bicarbonate species at 1650 cm^{-1} ($\nu_{\text{as}}(\text{CO}_3)$) and 1420 cm^{-1} ($\nu_{\text{s}}(\text{CO}_3)$) as well as bidentate bicarbonate species at 1515 cm^{-1} ($\nu_{\text{as}}(\text{CO}_3)$) and 1395 cm^{-1} ($\nu_{\text{s}}(\text{CO}_3)$) [59–61] (Fig. 8b). The absorption spectra showed no changes when the

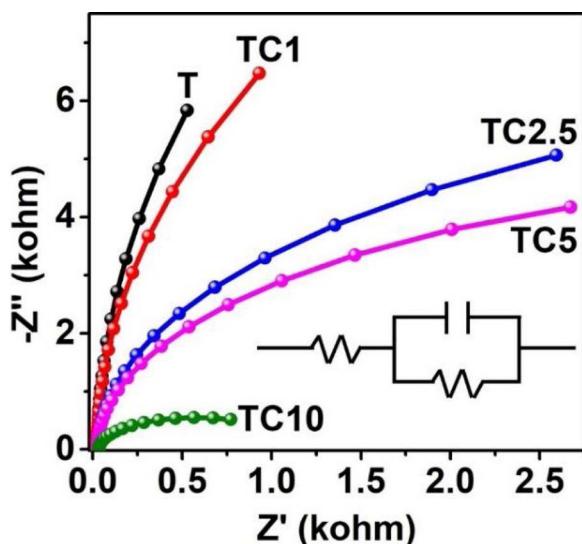


Fig. 9. Nyquist plots of the samples measured in 0.5 M Na_2SO_4 aqueous solution under Xe lamp irradiation.

exposure time was further increased to 40 and 60 min (Fig. 8c and d) without illumination. Under the photoirradiation, the intensities of monodentate and bidentate bicarbonate species increase with irradiation time (Fig. 8e–g) due to the large thermodynamic tendency for the conversion of $\text{CO}_2\text{--CO}_3^{2-}$. Meanwhile, some new absorption bands appear at 1540 and 1340 cm^{-1} , which are attributed to $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ of bidentate formic acid species [59]. The absorption bands located at 1456 and 1365 cm^{-1} are assigned to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ of absorbed formic acid species [60]. The bands at 1699 and 1740 cm^{-1} can be ascribed to $\nu_{\text{as}}(\text{CO})$ of absorbed formate and formic acid species, respectively [61]. It can be concluded that formate and formic acid were generated as the intermediates on the surface of $\text{TiO}_2/\text{CuInS}_2$ nanohybrids during the CO_2 reduction.

3.5. EIS measurement, EPR analysis and DFT calculation

Electrochemical impedance spectra (EIS) were measured to investigate the photogenerated charge transfer dynamics. Fig. 9 shows the EIS spectra of the samples and the semicircles observed in the Nyquist plots correspond to the charge transfer resistance in the sample/electrode interface. In general, a smaller semicircle implies a better charge transfer across this interface. As can be seen, the semicircle

became smaller as the content of CuInS_2 was increased, indicating that the hybridization with CuInS_2 was able to improve the electron transfer which thus led to a significant photocatalytic enhancement for the CO_2 reduction.

Moreover, terephthalic acid (TA) was used as a probe molecule to examine the $\cdot\text{OH}$ free radicals produced over the samples under illumination. The $\cdot\text{OH}$ radicals can easily react with TA to produce a luminescent TAOH adduct, with fluorescence emission centered at 425 nm. Hence, the corresponding photoluminescence (PL) spectra recorded after UV illumination for different time (0–60 min) over TC2.5 were recorded and shown in Fig. 10a. The PL intensity boosted with increasing irradiation time, implying the continuous generation of hydroxyl radicals upon TC2.5 under illumination. Fig. 10b shows the time courses of the PL intensity from TAOH for different samples. Clearly, TC2.5 generated the highest amount of $\cdot\text{OH}$ as compared to other samples and in contrast, while T showed minor PL increase even after 60 min illumination. Based on these results, we proposed a direct Z-scheme heterojunction formed between TiO_2 and CuInS_2 , i.e. the photo-generated electrons in the conduction band of TiO_2 can transfer to the valence band of CuInS_2 , reducing the recombination rate of electron/hole pairs and facilitating the production of $\cdot\text{OH}$ in aqueous solution. In the process of CO_2 reduction, we suppose that the $\cdot\text{OH}$ radicals were captured and quenched by the hydroxyl groups from TiO_2 [62,63].

The Z-scheme charge transfer pathway can be more directly evidenced by in-situ XPS measurement under light irradiation. As shown in Fig. 6b and c, the binding energies of Ti 2p and O 1s for TC2.5 under irradiation shifted positively by 0.2 eV as compared to the values in dark. Accordingly, the binding energies of Cu 2p and In 3d (Fig. 6d, e) for TC2.5 showed a negative shift of ca. 0.1 eV under irradiation. Such shifts clearly confirm the presence of electron transfer from TiO_2 to CuInS_2 under light irradiation driven by the direct Z-scheme heterojunction, agreeing well with the above analyses.

DFT calculations further confirm the generation of the Z-scheme heterostructure between TiO_2 and CuInS_2 . Generally, electrons will transfer from the semiconductor with higher Fermi energy (E_F) level to the other semiconductor with lower E_F level at the interface of two semiconductors. In our case, the E_F level of CuInS_2 is higher than that of TiO_2 (Fig. 11). This means the electrons can transfer from CuInS_2 to TiO_2 upon contact, creating a built-in electric field in the $\text{TiO}_2/\text{CuInS}_2$ interface with the orientation from CuInS_2 to TiO_2 upon contact. These analyses agree well with the XPS results as discussed above, that the electrons transfer from CuInS_2 to TiO_2 after hybridization to form a built-in electric field resulting from the shift of binding energies of Ti 2p, O 1s, Cu 2p and In 3d.

According to the above results and discussion, we propose a

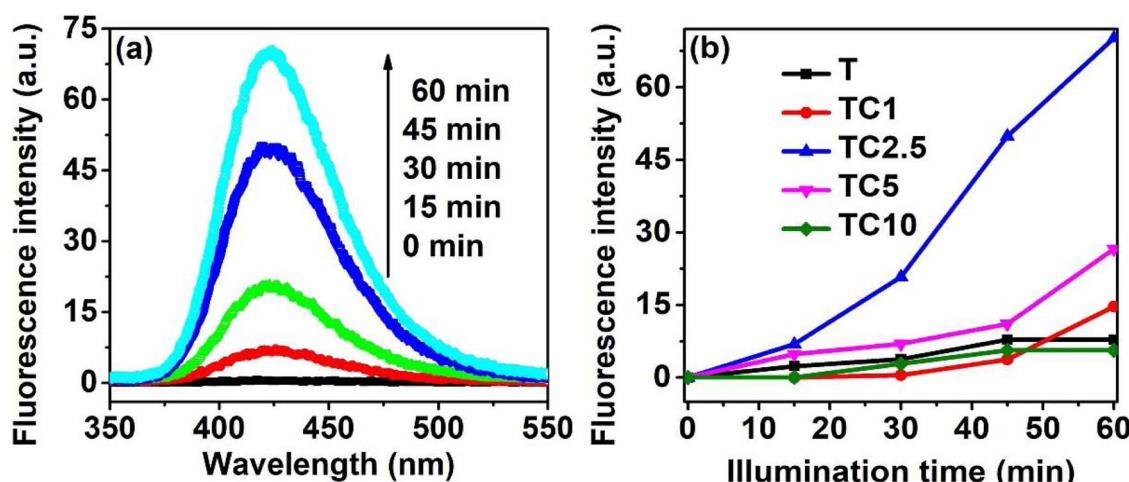


Fig. 10. (a) PL spectra of TA aqueous solution (5×10^{-4} M) in the presence of TC2.5 upon illumination for 0, 15, 30, 45 and 60 min. (b) PL intensity variation (425 nm) of the TA aqueous solution against time in the presence of different samples.

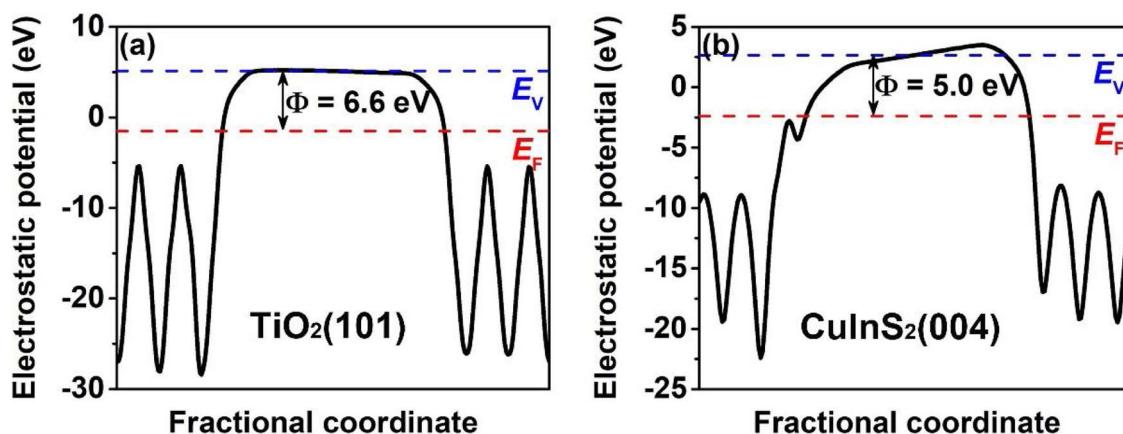


Fig. 11. Calculated electrostatic potentials for (a) TiO_2 (101) face and (b) CuInS_2 (004) face. The red and blue dashed lines denote Fermi level and the vacuum energy level, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

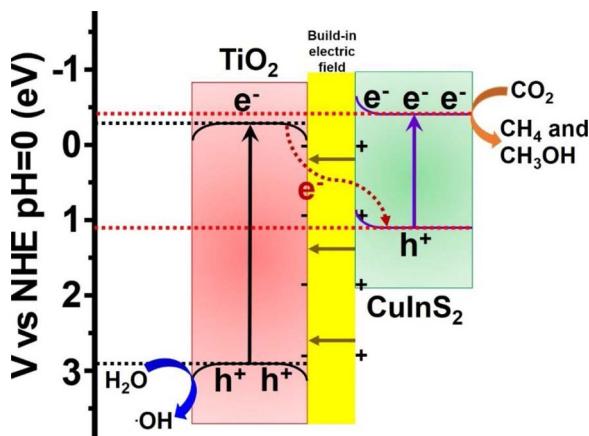


Fig. 12. Schematic illustration of the charge transfer and separation in TC2.5 under simulated sunlight light irradiation.

mechanism of the photocatalytic CO_2 reduction upon the hybrid materials. Under light irradiation, the electrons in the valence band (VB) of TiO_2 and CuInS_2 were excited to the conduction band (CB). Owing to the presence of the internal electric field pointing from CuInS_2 to TiO_2 , the electrons in TiO_2 CB would transfer and recombine with the holes in CuInS_2 VB, instead of the electrons in CuInS_2 CB transfer to TiO_2 CB. This Z-scheme configuration can improve the separation and extraction of the charge carriers (electrons from CuInS_2 and holes from TiO_2) [64–66]. Therefore, the photo-induced electrons from CuInS_2 CB would react with the adsorbed CO_2 molecules, with the CO_2 reduced to CH_4 and CH_3OH with water as the proton source [67–69]. The photocatalytic mechanism and the charge transfer for the $\text{TiO}_2/\text{CuInS}_2$ Z-scheme heterostructures are schematically illustrated in Fig. 12.

4. Conclusions

In summary, novel $\text{TiO}_2/\text{CuInS}_2$ core-shell nanofibers were fabricated through an electrospinning and subsequent hydrothermal methods. The resulting $\text{TiO}_2/\text{CuInS}_2$ hybrid nanofibers exhibit superior photocatalytic activity for CO_2 reduction under irradiation, due to the enhanced light absorption, increased surface area and most importantly, the generation of Z-scheme heterojunction between TiO_2 and CuInS_2 . The formation of the Z-scheme heterojunction was verified by XPS measurement, DFT calculation and free radical analysis. The direct Z-scheme heterojunction could significantly promote the charge separation and extraction upon photo-excitation, resulting in improved hydrocarbon production from CO_2 reduction. Our work provides a new insight into the design and synthesis of TiO_2 -based photocatalysts with

Z-scheme pathways for high-efficiency solar-fuel conversion.

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